paper chromatography that demethylation of MHB *in vivo* took place in mice. However, these two products were not detected in our experiment.

The quantitative investigation on the metabolites of MHB will be reported in the following paper.

Summary

Examination of urinary product of rabbits administered with MHB, by filter paper chromatography, indicated that ureide, 3-OH-MHB, 3-keto-MHB, 3-keto-nor-MHB, and unknown compounds (MHB-M (VI)) were excreted.

An excellent method for the separation of these compounds is the use of a buffered filter paper and butanol saturated with borate-NaOH buffer (pH 11).

For detection of the located metabolites, 1% solution of sodium periodate and 1% solution of potassium permanganate were used and ultraviolet spectrophotometry was adopted for the characterization of barbiturates.

(Received September 2, 1957)

UDC 547.673.1 : 544.621

5. **Osamu Tanaka**: Infrared Spectra of Anthraquinone Derivatives. I. The Effect of Hydroxyl, Acetoxyl, Methoxyl, and Methyl Substitutions on the C=O Stretching Frequency.

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Although some infrared spectral studies on anthraquinone derivatives were previously reported by Flett,[1] Josien *et al.*,[2,3] Wiles,[4] and some other workers,[5] more extensive studies are required to provide a precise information applicable to the chemistry of naturally occurring anthraquinones and their related compounds.

For this purpose, supplementing the previously published data, the present author carried out a measurement of infrared spectra of about 80 anthraquinone derivatives to examine the correlation of C=O stretching frequency to the substituents such as the hydroxyl, methoxyl, and methyl groupings.

It is well-known that change of the state of a sample sometimes causes a shift of C=O frequency, which must be ascribed to intermolecular forces. For quinoid compounds, Josien and her co-workers[2] observed that an anomalous diminution in C=O frequency sometimes occurs in the condensed phase compared to that in non-polar solvents such as carbon tetrachloride and carbon disulfide. Therefore, the measurement of infrared spectra in the solid state is not suitable for the present purpose. However, carbon tetrachloride and carbon disulfide are not suitable as a solvent, since anthraquinones in general, especially their hydroxyl derivatives, are very sparingly soluble in these solvents.

The effect of dioxane as a solvent for infrared spectral measurement has been

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* Hongo, Tokyo (田中 治).

[1] M. St. Flett: J. Chem. Soc. **1948**, 1441.

[2] M-L. Josien, N. Fuson: Bull. soc. chim. France, **1952**, 389.

[3] M-L. Josien, N. Fuson, J-M. Lebas, T.M. Gregory: J. Chem. Phys., **21**, 331(1953).

[4] L.A. Wiles, L.C. Thomas: J. Chem. Soc., **1956**, 4811.

[5] D. Hadzi, N. Sheppard: Trans. Farady Soc., **50**, 911(1954); H. Hoyer: Chem. Ber., **86**, 1016 (1953); D.N. Shigorin, N.S. Dokunikhin: Zhur. Fiz. Khim., **29**, 1958(1955) (C.A., **49**, 14485(1956)).

examined. Dioxane, as a strong proton acceptor, forms a solvent-solute complex with compounds containing a proton-donating group, such as the hydroxyl, causing a shift of O-H stretching band to a lower wave number. For instance, the carboxylic acids which associate to form a dimer in the condensed phase, exhibit a shift of C=O and O-H stretching bands in dioxane solution, which is attributed to the formation of a dioxane-carboxylic acid complex. Similar results may be expected in other hydroxy-carbonyl compounds which associate in crystalline state through hydrogen bonding. On the other hand, Hartwell, *et al.*[6] reported that no remakably different effect was observed for the C=O band of simple carbonyl compounds in dioxane as in carbon disulfide and carbon tetrachloride. On the effect of substituents to C=O frequency of hydroxy-phthalide derivatives, Grove, *et al.*[7] showed that dioxane gave a more distinct regularity in the results than that in chloroform or in a solid state. Similar result was noted by Shibata[8] for strepsilin and its related compounds.

Consequently, it becomes clear that for discussion of the effect of substitution to the C=O frequency of anthraquinone derivatives, dioxane can be used as the solvent in which most of the anthraquinones, except polyhydroxyl derivatives, are soluble to form the solution of a suitable concentration. The complicated intermolecular interaction which is inevitably shown in the crystalline state need not be considered in the dioxane solution.

For comparison with the results obtained in the solution, spectra in the solid state were also examined. The results are shown in Tables I～V.

Results and Discussion

It has been observed that the C=O frequencies of aromatic carbonyl compounds such as benzophenones and acetophenones are affected by the substitution in the aromatic ring. The relationship between the shift in C=O band and Hammett's substitution constant has also been discussed. In general, amino or nitro substitution cause a considerble alteration in C=O frequencies, and *p*-methoxyl or *p*-hydroxyl group also displaces the C=O band by about $5\sim10\,\mathrm{cm}^{-1}$ to a lower wave number. Similar effect has been reported in quinoid compounds, but the influence of substituents to C=O frequencies is much more complicated in the case of benzoquinones and naphthoquinones, and seems to be still controversial.[9]

For anthraquinone derivatives, Flett[1] and Josien, *et al.*[2,3] examined the spectra of some compounds and recently, Wiles and his associate[4] observed in the spectra of some methoxyanthraquinones in CCl_4 or $CHCl_3$ solution that the β-methoxyl group caused a marked diminution in C=O frequency compared to the α-methoxyl group, and if both carbonyl groups were affected by the β-methoxyl groups at *para*-position, the diminution was most distinct.

Free C=O Frequency (The stretching-vibration frequency due to the carbonyl group not chelated with α-hydroxyl groups)

Examination in the solid state—With anthraquinone itself, C=O band appears at $1670\,\mathrm{cm}^{-1}$. In the present measurement, most compounds showed the free C=O band within the range of $1672\pm4\,\mathrm{cm}^{-1}$ (Table I), but in the following case, marked changes were observed.

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[6] E.J. Hartwell, H.W. Thompson, R.E. Richards : J. Chem. Soc., **1948**, 1436.
[7] L.A. Duncanson, J.F. Grove, J. Zealley : *Ibid.*, **1953**, 1331.
[8] S. Shibata : This Bulletin, **5**, 50(1957).
[9] M-L. Josien, J. Deschamps : J. chim. phys., **52**, 213(1955); P. Yates, M.I. Ardas, L.F. Fieser: J. Am. Chem. Soc., **78**, 650(1956); M-L. Josien, J. Deschamps : Compt. rend., **242**, 3067(1956).

TABLE I. The Free C=O Stretching Band of Anthraquinone Derivatives

Following compounds show the free C=O band at 1672±4 cm^{-1} in the solid state and at 1676±3 cm^{-1} in the dioxane solution :

1) Acetoxy, methyl, and monomethoxy derivatives : 1-OAc-, 1,2-(OAc)$_2$-, 1,3-(OAc)$_2$-, [1,4-(OAc)$_2$-], 2,3-(OAc)$_2$-, 1,2,4-(OAc)$_3$-, [1,2,5,8-(OAc)$_4$-], 2-CH$_3$-(1676 cm^{-1} in CCl$_4$), [1-OAc-3-CH$_3$-], 1,4-(OAc)$_2$-2-CH$_3$-, [1,3,8-(OAc)$_3$-6-CH$_3$-], 1-OCH$_3$-(1673 cm^{-1} in CHCl$_3$, 1675 cm^{-1} in CCl$_4$), 2-OAc-4-OCH$_3$-, [2-OCH$_3$-], 1-OAc-2-OCH$_3$-, 1-OAc-3-OCH$_3$-, and [2-OCH$_3$-3-CH$_3$-]-anthraquinones.
2) Di- or poly-methoxy derivatives : 1,2-(OCH$_3$)$_2$- and [1,4-(OCH$_3$)$_2$-(1675 cm^{-1} in CCl$_4$)]-anthraquinones.
3) α-Monohydroxy derivatives : 1-OH-(1675 cm^{-1} in CCl$_4$), 2-OAc-1-OH-, 2-OAc-4-OH-, [1-OH-3-CH$_3$-] and 2-OAc-4-OH-3-CH$_3$- anthraquinones.
4) α-Monohydroxy-methoxy derivatives : 1-OH-8-OCH$_3$-, 1-OH-3-OCH$_3$-, and 1-OH-3-OCH$_3$-2-CH$_3$- anthraquinones.
5) α-Monohydroxy-β-hydroxy derivative : 1,3-(OH)$_2$- anthraquinone.
6) 1,8-Dihydroxy derivatives : 1,8-(OH)$_2$-, 1,8-(OH)$_2$-2-CH$_3$-, 1,8-(OH)$_2$-3-CH$_3$-, and 1,8-(OH)$_2$-3-OCH$_3$-6-CH$_3$- anthraquinones.

The compounds in brackets were not examined in the dioxane solution.

TABLE II. The Free C=O Stretching Band of Anthraquinone Derivatives

In the following compounds, the free C=O band appears at 1676±3 cm^{-1} in the dioxane solution, but this band shifts to a lower frequency from that in Table I, or the anomalous changes occur in the solid state, (The wave number shows the position of absorption maximum observed as a solid).

1) Acetoxy, Methyl derivatives : 1,8-(OAc)$_2$- 1669, 1678 cm^{-1}(1677 cm^{-1} in CHCl$_3$) and 1,8-(OAc)$_2$-3-CH$_3$-anthraquinones 1667, 1680 cm^{-1}.
2) Di- or poly- methoxy derivatives : 1,3-(OCH$_3$)$_2$-2-CH$_3$- 1666 cm^{-1}, 1,8-(OCH$_3$)$_2$- 1660 cm^{-1}, 1,8-(OCH$_3$)$_2$-3-CH$_3$- 1661 cm^{-1}(1669 cm^{-1} in CHCl$_3$), 1,3,8-(OCH$_3$)$_3$-6-CH$_3$- 1655 cm^{-1}, [1,4,5-(OCH$_3$)$_3$-2-CH$_3$- 1664 cm^{-1}], 1,2,5,8-(OCH$_3$)$_4$- 1666 cm^{-1}, and 1,2,4,5-(OCH$_3$)$_4$-7-CH$_3$-anthraquinones 1658 cm^{-1}.
3) β-Hydroxy derivatives : 2-OH- 1666 cm^{-1}, [2-OH-4-OCH$_3$- 1673, 1641 cm^{-1}], 2-OH-4-OCH$_3$-3-CH$_3$- 1674, 1650 cm^{-1}, 2-OH-4-OCH$_3$-3-CH$_2$OH-(damnacanthol) 1665, 1643 cm^{-1}, and 2-OH-4,5-(OCH$_3$)$_2$-7-CH$_3$-anthraquinones (4,5-dimethylemodin) 1670, 1648 cm^{-1}.
4) α-Monohydroxy-methoxy derivative : 1-OH-4-OCH$_3$-anthraquinone 1659 cm^{-1}.
5) α-Monohydroxy-β-hydroxy derivative : 1,3-(OH)$_2$-2-CH$_3$-anthraquinone 1662 cm^{-1}.
6) 1,8-Dihydroxy derivative : 1,3,8-(OH)$_3$-6-CH$_3$-anthraquinone 1665 cm^{-1}.

The compounds in brackets were not examined in the dioxane solution.

TABLE III. The Free C=O Stretching Band of Anthraquinone Derivatives

Following compounds show a diminution in the free C=O frequency in the dioxane solution as well as in the solid state.

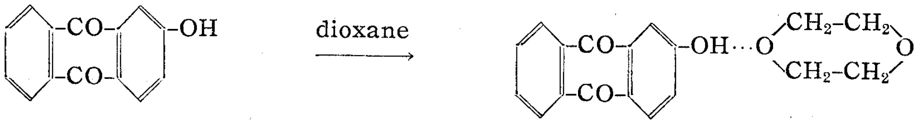
Compound	Free C=O frequency (in cm^{-1})		Notes
	as a solid	in dioxane	
1) Di or poly-methoxy derivatives			
1,3-(OCH$_3$)$_2$-anthraquinone	1660	1670	1667 in CHCl$_3$ 1674 in CCl$_4$
1,2,3-(OCH$_3$)$_3$- 〃	1671	1670	
1,5-(OCH$_3$)$_2$- 〃	1662	1669	
2) β-Hydroxy derivatives			
2,3-(OH)$_2$-anthraquinone	1668	1672	
2,6-(OH)$_2$- 〃	1658	1670	
3) α-Monohydroxy-methoxy derivatives			
1-OH-2-OCH$_3$-anthraquinone	1669	1666	
1-OH-2,3-(OCH$_3$)$_2$- 〃	1669	1670	
4) α-Monohydroxy-β-hydroxy derivatives			
1,2-(OH)$_2$-anthraquinone	1659	1664	
1,2,3-(OH)$_3$- 〃	1655	1670	
1,7-(OH)$_2$-3-CH$_3$- 〃	not observed	1670	
1,7-(OH)$_2$-5-CH$_3$- 〃	1664	1671	

Some of the di- or poly-methoxy derivatives (Table II (-2), III (-1)) show a diminution in free C=O frequency by 2~15 cm^{-1}, and in most compounds containing β-hydroxyl group (Table II (-3, 5, 6), III (-2, 4)), free C=O band also shifts to a lower frequency by about 2~12 cm^{-1}. In the case of 2-OH-4-OCH_3-, 2-OH-4-OCH_3-3-CH_3-, 2-OH-4-OCH_3-3-CH_2-OH-(damnacanthol),[10] 2-OH-4,5-$(OCH_3)_2$-7-CH_3-anthraquinones (4,5-dimethylemodin), an additional band appears in the region of 1650~1640 cm^{-1} besides that at the normal position. These spectra are indistinguishable from that of the compounds which have one α-hydroxyl group or are contaminated with some impurities possessing a chelated carbonyl group. 1,7-$(OH)_2$-3-CH_3-anthraquinone gives no absorption in the region of 1675~1665 cm^{-1}, and shows only a chelated C=O band at 1639 cm^{-1}.

Although these phenomena appear to be explainable by the consideration of the mesomeric effect of methoxyl or hydroxyl groups to the free carbonyl group, any definitely generalized conclusion concerning the infiuence of these substituents on free C=O frequency cannot be given by observation in the solid state.

Examination in the dioxane solution—In dioxane, free C=O band moves to a slightly higher frequency than in the solid state and most compounds examined (Table I, II) gave the free C=O absorption at 1676±3 cm^{-1}. This absorption range shows no appreciable difference from those in CCl_4 and CS_2 solutions reported by Flett and by Josien and her associates on some anthraquinone derivatives. It is clear that acetoxyl, methyl, or one methoxyl group causes little effect on the free C=O frequency.

In dioxane, the mesomeric effect of β-hydroxyl group may be increased by the formation of a dioxane-solute complex.* Nevertheless, β-hydroxy derivatives show neither a marked decrease in free C=O frequency nor an anomalous additional band observed in the spectra measured in the crystalline state, and occurrence of the shift in free C=O band is confined to a few compounds listed in Table III (-2,4). From these results, it is clear that the mesomeric effect of β-hydroxyl group plays only a relatively small part in the displacement of free C=O frequency in the solid state, and the major effect is probably the strong intermolecular association through the hydrogen bonding occurring in the crystalline form. The presence of a strong intermolecular hydrogen bond in the β-hydroxyanthraquinone derivatives was pointed out by Flett[1] from the facts that O-H stretching band of these compounds appeared in the region of 3400~3300 cm^{-1} (sometimes near 3200 cm^{-1}) and all of these compounds had high melting point (250~360°) and low solubility in ordinary organic solvents.



Similar observations are obtained in the case of di- or poly-methoxyl derivatives, and it is also suggested that the free C=O frequency of these compounds is sometimes affected considerably by the strong intermolecular forces in the crystalline state.

In some of the acetoxy-methyl derivatives, free C=O band has two submaxima in the solid state, but in dioxane this becomes a sharp one in the normal position (Table II (-1)).

However, the influence of β-methoxyl and β-hydroxyl groups to the free C=O frequency appears to some extent in the compounds described below. The observation on the di- or poly-methoxy derivatives in the dioxane solution is almost in accord

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* In dioxane, the stretching vibration band of β-O-H bond appears near 3250 cm^{-1} for all β-hydroxy derivatives.

[10] S. Nonomura: Yakugaku Zasshi, **75**, 219, 222, 225(1955); S. Nonomura, Y. Hirose: *Ibid.*, **75**, 1305(1955); Y. Hirose: *Ibid.*, **76**, 1448(1956).

with the Wiles' investigation,[4] and the author notes that a similar tendency exists in β-hydroxy derivatives (Table III (-2)).

In these compounds where both carbonyl groups are free, the effect of one methoxyl or hydroxyl group on the two C=O bonding might be different. Nevertheless, only a single C=O band is observed. For these reasons, the relationship between the free C=O frequency and substituents appears to be rather complicated and it may be difficult to illustrate the correlation in a simple term.

When one carbonyl group is chelated with the α-hydroxyl group and only one carbonyl group is free, one C=O vibration absorption is attributed to the free C=O band and the correlation is more simplified than in the above cases. In this case the hydroxyl or methoxyl subsitution at the position *para* to the free carbonyl displaces the free C=O frequency by about $6\sim10\,cm^{-1}$ to a lower wave number (Table III (-3, 4)).

In general, the intensity of the free C=O band is weaker than that of chelated C=O band, and especially in the case of $1,3,8\text{-}(OH)_3\text{-}6\text{-}CH_3$- and $1,8\text{-}(OH)_2\text{-}3\text{-}OCH_3\text{-}6\text{-}CH_3$-anthraquinones, the absorption band near $1676\,cm^{-1}$ is so weak that it is doubtful whether this absorption is accurately due to a stretching vibration of free C=O or not.[11] On the contrary, in $1,2\text{-}(OH)_2$-anthraquinone (alizarin), which is a well-known mordant dye, the free C=O band is stronger than a chelated C=O band both in the solid and in the dioxane solution. It would be interesting to study the relationship between the absolute intensity of a C=O band and substituents, but the present work does not deal with this problem in detail.

Chelated C=O Frequency (The stretching-vibration frequency due to the carbonyl group chelated with α-hydroxyl groups)

It has been already reported by Flett and many other workers that the hydroxyl group at the α-position of anthraquinone forms a strong conjugated chelation system with the carbonyl group, causing a considerable decrease in the C=O frequency by $30\sim70\,cm^{-1}$. However, all of the previous studies on the infrared spectra of these compounds have been carried out in the crystalline state and the correlation of chelated C=O frequency with substituents has not fully been elucidated. A measurement in the crystalline phase gives no precise correlation whereas the observation in dioxane offers the useful regularity in the relationship between the chelated C=O frequency and the substitutions.

The compounds which possess one chelated carbonyl group but no hydroxyl or methoxyl groups at the position *para* to the chelated carbonyl group (Table IV (-1, 2)) all show a chelated C=O absorption band at $1642\pm2\,cm^{-1}$.

If the methoxyl or hydroxyl substitution occurred at the position *para* to the chel-

TABLE IV. The Chelated C=O Stretching Band of Anthraquinone Derivatives

In the following compounds, the chelated C=O band appears at $1642\pm2\,cm^{-1}$ in the dioxane solution.

Compound	Chelated C=O frequency (in cm^{-1}) as a solid	in dioxane	Notes
1) α-Monohydroxy derivatives			
1-OH-anthraquinone	1635	1642	1639 in CCl_4
2-OAc-1-OH- 〃	1640	1642	
2-OAc-4-OH- 〃	1645	1640	
2-OAc-4-OH-3-CH_3- 〃	1630	1643	
2) α-Monohydroxy-methoxy derivatives			
1-OH-2-OCH_3-anthraquinone	1644	1640	
1-OH-4-OCH_3- 〃	1638	1644	
1-OH-8-OCH_3- 〃	1633	1640	

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[11] cf. B.H. Howard, H. Raistrick: Biochem. J., **59**, 475(1955).

Table V. The Chelated C=O Stretching Band of Anthraquinone Derivatives

Following compounds show a diminution in the chelated C=O frequency from that in Table IV in the dioxane solution.

Compound	Chelated C=O frequency (in cm^{-1})	
	as a solid	in dioxane
1) α-Monohydroxy-methoxy derivatives		
1-OH-3-OCH_3-anthraquinone	1627	1633
1-OH-3-OCH_3-2-CH_3- 〃	1628	1632
1-OH-2,3-$(OCH_3)_2$- 〃	1631	1632
2) α-Monohydroxy-β-hydroxy derivatives		
1,3-$(OH)_2$-anthraquinone	1638	1632
1,3-$(OH)_2$-2-CH_3- 〃	1625	1631
(1,2-$(OH)_2$- 〃	1631	1635)
1,2,3-$(OH)_3$- 〃	1624	1632
3) 1,4-Dihydroxy derivatives		
1,4-$(OH)_2$-anthraquinone	1630	1631
1,4-$(OH)_2$-2-CH_3- 〃	1630	1626
1,4-$(OH)_2$-2-OCH_3- 〃	1617	1623
1,2,4-$(OH)_3$- 〃	1622	1624
4) 1,8-Dihydroxy derivatives	1625	1632
1,8-$(OH)_2$-anthraquinone	1625	1632
1,8-$(OH)_2$-2-CH_3- 〃	ca. 1620	1629
1,8-$(OH)_2$-3-CH_3- 〃	1627	1631
1,8-$(OH)_2$-3-OCH_3-6-CH_3- 〃	ca. 1628	1627
1,3,8-$(OH)_3$-6-CH_3- 〃	ca. 1620	1630
5) 1,5-Dihydroxy derivatives		
1,5-$(OH)_2$-anthraquinone	1631	1632
(1,5-$(OH)_2$-3-CH_3- 〃	ca. 1618)	
(1,5-$(OH)_2$-2-CH_3- 〃	ca. 1624)	
(1,5-$(OH)_2$-2,3,6,7-$(OCH_3)_4$- 〃	ca. 1630)	
(1,2,3,5,6,7,-$(OH)_6$- 〃 〃	ca. 1595)	
6) α-Trihydroxy derivatives		
1,4,5-$(OH)_3$-2-CH_3-anthraquinone	ca. 1597	ca. 1604
(1,4,5,7-$(OH)_4$-2-CH_3- 〃	ca. 1600)	
(1,4,5-$(OH)_3$-7-OCH_3-2-CH_3- 〃	ca. 1598)	
(1,4,5-$(OH)_3$-2-OCH_3-7-CH_3- 〃	ca. 1606)	

ated carbonyl group, the band moves to 1631±2 cm^{-1} (Table V (-1, 2)). This lowering may be attributed to the mesomeric effect of the hydroxyl or methoxyl group on the C=O linkage.

For the quinizarin-type (1,4-dihydroxy-type) compounds (Table V (-3)), a similar decrease of the chelated C=O frequency takes place and the introduction of β-hydroxyl or β-methoxyl group gives rise to further diminution of this band. This observation suggests that a stronger conjugated chelation system exists in these compounds.

In 1,2-$(OH)_2$-anthraquinone, chelated C=O band appears at 1635 cm^{-1} which is slightly weaker than that of the free C=O band.

In 1,8- or 1,5-dihydroxy derivatives (Table V (-4, 5)), owing to the considerable increase of the frequency of the anthraquinone ring vibration (phenyl band), the chelated C=O band is sometimes overlapped with this phenyl band in the solid state measurement, and in many cases, exact determination of the chelated C=O band seems to be impossible. In dioxane, the spectra of many compounds show a sharper chelated C=O band near 1630 cm^{-1}, which indicates the presence of a stronger conjugated hydrogen bonding; in this case, the phenyl band appears as a peak on the low frequency side of chelated C=O band. However, for some compounds, the spectra either in the solid or in dioxane give only a strong broad band near 1620 cm^{-1} which is presumably associated with the chelated C=O and phenyl bands. In most α-polyhydroxy derivatives, where a marked lowering of a chelated C=O frequency is expected, the strong broad band near 1610~1590 cm^{-1} probably also includes the chelated C=O absorption and phenyl bands. For this reason, it may be impossible to make a satisfactory assignment of the chelated C=O band in these compounds.

Further report on the phenyl band of anthraquinone derivatives will be made in a subsequent paper.

The author wishes to acknowledge the encouragement and helpful advices of Prof. S. Shibata. The infrared measurement was carried out in the Central Clinical laboratory of the Tokyo University Hospital, to the members of which the author's thanks are due. The author is also indebted to Messrs. J. Shoji and T. Tanikawa for their help in the measurement of infrared spectra.

Experimental

Substances examined were prepared by known methods and carefully purified before use. Some of the samples were provided by Mr. M. Takido of the Nihon University and Mr. Y. Hirose of the University of Kumamoto to whom the author is grateful for their kindness. 2-OH-4,5-$(OCH_3)_2$-7-CH_3-anthraquinone (4,5-dimethylemodin) is a new compound which was prepared by the reductive cleavage of diacetyltetramethylskyrin; the details of the preparation methods and physical properties of these compounds will be described in a forthcoming report.

Infrared spectra were measured by a Hilger H 800 double-beam spectrometer fitted with a rock-salt prism. For measurement as a solid, the Nujol mull technique was used. The spectra in dioxane were measured in 1~2% solution (if the sample is only slightly soluble in this solvent, a saturated solution was used), with the cell of 0.1 mm. thickness. A change of the concentration between 0.5% and 2.0% did not affect the position of C=O absorption maximum. For a few compounds, spectra in dilute solution in CCl_4 or $CHCl_3$ were also examined. The data were always carefully corrected by comparing with the absorption maxima of polystyrene film.

Summary

The infrared spectra of about 80 anthraquinone derivatives substituted with acetoxyl, hydroxyl, methoxyl, or methyl group, were measured in the dioxane solution and in the solid state. The effect of substituents on the free and chelated C=O stretching vibration frequencies was discussed.

(Received September 5, 1957)

UDC 547.673.1 : 544.621

6. **Osamu Tanaka**: Infrared Spectra of Anthraquinone Derivatives. II.* The Relationship between the Absorption Bands in the Region of 1480~1620 cm^{-1} and Hydroxyl, Methoxyl, Acetoxyl, and Methyl Substitutions.

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It has been well known that compounds containing an aromatic ring show skeletal vibration bands within the range of 1480~1620 cm^{-1} (phenyl band) and conjugation of the aromatic ring with C=O, C=C, etc. causes increase of the intensity of these bands.[1~3] Bomstein[4] examined the effect of substituents on the intensity of the phenyl band near 1600 cm^{-1} for the mono- and di-substituted benzene derivatives and reported that the directing influence and orientation of substituents in the ring are the most important factors. However, extensive systematic studies on the phenyl bands of a more complex molecules have not been made.

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* Part I: O. Tanaka: This Bulletin, **6**, 18(1958).

** Hongo, Tokyo (田中 治).

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3) M-L. Josien, J-M. Lebas: Bull. soc. chim. France, **1956**, 53, 57.

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